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ELEMENT SEPARATING INSULATION FILM AND FORMATION METHOD THEREOF

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ELEMENT SEPARATING INSULATION FILM AND FORMATION METHOD THEREOF

[Soshi bunri zetsuenmaku oyobi sono keisei hoho]

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Claims

1. A type of element separating insulation film characterized by the fact that

the element separating insulation film made of oxide film for separating elements of a semiconductor device contains 5-20 atom% of fluorine atoms.

2. A method for forming element separating insulation film characterized by the fact that

in the method for forming element separating insulation film, in which an oxide film is formed on a silicon substrate by means of a selective oxidation method by means of a silicon nitride film used as an oxidation inhibiting mask,

fluorine gas or a gas containing fluorine is fed into a selective oxidation atmosphere for forming the oxide film to selectively oxidize for the aforementioned silicon substrate, so as to form an oxide film on the silicon substrate.

3. A method for forming element separating insulation film characterized by the fact that

in the method for forming element separating insulation film, in which an oxide film is formed on a silicon substrate by

means of a selective oxidation method by means of a silicon nitride film used as an oxidation inhibiting mask,

after an oxide film is formed on the silicon substrate by means of selective oxidation of the aforementioned silicon substrate, fluorine ions or ions containing fluorine are selectively introduced into the oxide film.

4. A method for forming element separating insulation film characterized by the fact that

in the method for forming element separating insulation film, in which an oxide film is formed on a silicon substrate by means of a selective oxidation method by means of a silicon nitride film used as an oxidation inhibiting mask,

after formation of the aforementioned oxidation inhibiting mask and before performing the aforementioned selective oxidation, fluorine ions or ions containing fluorine are selectively introduced into the region of the silicon substrate where the oxide film is to to be formed, followed by selective oxidation so as to form the oxide film on the aforementioned region where the oxide film is to be formed.

Detailed explanation of the invention

[0001]

Industrial application field

This invention pertains to a type of element separating insulation film and its formation method. In particular, this invention pertains to a type of element separating insulation film, which has a low dielectric constant and is appropriate for

use in the semiconductor IC of memory elements having advanced integration degree, and its formation method.

[0002]

Prior art

Most element separating insulation films for semiconductor devices are formed using LOCOS oxidation method. In the LOCOS oxidation method, after a pad silicon oxide film is formed on the surface of a silicon substrate, the silicon oxide film is patterned to form an oxidation inhibiting mask. Then, the surface of the silicon substrate is subjected to selective oxidation to form a LOCOS oxide film.

[0003]

In the aforementioned LOCOS oxidation method, the oxide film extends in the direction of the substrate plane at the silicon nitride film edge portion, leading to so-called bird's beak phenomenon. The bird's beak phenomenon is one of the factors that jeopardize the efforts to form finer semiconductor devices. As shown in Figure 6, a portion of the surface layer of silicon substrate (101) is oxidized using the LOCOS oxidation method. In particular, in narrow active region (102) with width of 0.35 μm or smaller, bird's beaks (112B) and (113B) of LOCOS oxide films (112), (113) grown from below the two end sides of silicon nitride film (111a) (111) become overlapped with each other, so that film thickness d1 of this portion becomes larger than film thickness D2 of existing pad silicon oxide film (114).

[0004]

After silicon nitride film (111) is etched off, active region (102) is formed on silicon substrate (101) below the portion where said bird's beaks (112B) and (113B) extend. For this purpose, bird's beaks (112B) and (113B) are etched off to expose the surface of silicon substrate (101).

[0005]

Problems to be solved by the invention

However, as shown in Figure 7, the film thickness of bird's beaks (112B) and (113B) (the portions indicated by double-dot-dash lines) extending to the region where active region (102) is formed is larger than the film thickness of pad silicon oxide film (114) (the portion indicated by single dot-dash lines) where the bird's beaks do not extend. Consequently, when bird's beaks (112B) and (113B) are etched off together with pad silicon oxide film film (114), the upper layers of LOCOS oxide films (112) and (113) (the portions indicated by broken lines) are also removed by nearly the same thickness as the thickness of bird's beaks (112B) and (113B). As a result, film thickness D2 of LOCOS oxide films (112) and (113) becomes smaller tan design value D1. Also, while not shown in the figure, there is also a method in which the film thickness of the LOCOS oxide film itself is reduced to form a narrow active region. However, in this method, too, the film thickness of the LOCOS oxide film becomes smaller. As the LOCOS oxide film become thinner, the parasitic capacitance rises. Consequently, the delay

time becomes longer, and the operation speed of the circuit becomes lower.

[0006]

The purpose of this invention is to provide a type of element separating insulation film, which has excellent effect for forming finer [semiconductor devices] with low parasitic capacitance, and its forming method.

[0007]

Means to solve the problems

This invention provides a type of element separating insulation film and its forming method to realize the aforementioned purpose. The element separating insulation film of this invention is made of an oxide film, which contains 5-20 atomic% of fluorine atoms.

[0008]

In the first method for forming the element separating insulation film, in which an oxide film is formed on a silicon substrate by means of a selective oxidation method by means of a silicon nitride film used as an oxidation inhibiting mask, fluorine gas or a gas containing fluorine is fed into a selective oxidation atmosphere for forming the oxide film to perform selective oxidation for the aforementioned silicon substrate, so as to form an oxide film on the silicon substrate.

[0009]

In the second method for forming the element separating insulation film, in which an oxide film is formed on a silicon substrate by means of a selective oxidation method by means of a silicon nitride film used as an oxidation inhibiting mask, after an oxide film is formed on the silicon substrate by means of selective oxidation of the aforementioned silicon substrate, fluorine ions or ions containing fluorine are selectively introduced into the oxide film.

[0010]

In the third method for forming the element separating insulation film, in which an oxide film is formed on a silicon substrate by means of a selective oxidation method by means of a silicon nitride film used as an oxidation inhibiting mask, after formation of the aforementioned oxidation inhibiting mask and before performing the aforementioned selective oxidation, fluorine ions or ions containing fluorine are selectively introduced into the region of the silicon substrate where the oxide film is to to be formed, followed by selective oxidation so as to form the oxide film on the aforementioned region where the oxide film is to be formed.

[0011]

Function

In the aforementioned element separating insulation film, the conent of fluorine atoms in the oxide film is in the range of 5-20 atom%. Consequently, the dielectric constant becomes lower than that of the oxide film free of the fluorine atoms (4.2). The dielectric constant of the film depends on the content of the fluorine atoms and is in the range of 3.0-3.5. Also, if the content of the fluorine atoms is less than 5 atom%, the dielectric constant of the oxide film is not reduced sufficiently. On the other hand, if the content of fluorine atoms is over 20 atom%, the fluorine atoms in the film become nearly saturated, so that fluorine makes reaction with hydrogen in the atmosphere to form hydrogen fluoride. In this case, hydrogen fluoride causes corrosion of the aluminum based wiring formed on the element separating insulation film. The corrosion may even lead to breakage of wires. Consequently, the content of the fluorine atoms should be within the aforementioned range.

[0012]

In the first method for forming the element separating insulation film, in which an oxide film is formed on a silicon substrate by means of a selective oxidation method by means of a silicon nitride film used as an oxidation inhibiting mask, fluorine gas or a gas containing fluorine is fed into a selective oxidation atmosphere for forming the oxide film to perform selective oxidation for the aforementioned silicon substrate, so

as to form an oxide film on the silicon substrate. In this way, fluorine atoms are contained in the oxide film formed on the silicon substrate.

[0013]

In the second method for forming the element separating insulation film, in which an oxide film is formed on a silicon substrate by means of a selective oxidation method by means of a silicon nitride film used as an oxidation inhibiting mask, after an oxide film is formed on the silicon substrate by means of selective oxidation of the aforementioned silicon substrate, fluorine ions or ions containing fluorine are selectively introduced into the oxide film. In this way, fluorine is not introduced into the portion of the silicon substrate which is to become the active region covered by the oxidation inhibiting mask.

[0014]

In the third method for forming the element separating insulation film, in which an oxide film is formed on a silicon substrate by means of a selective oxidation method by means of a silicon nitride film used as an oxidation inhibiting mask, after formation of the aforementioned oxidation inhibiting mask and before performing the aforementioned selective oxidation, fluorine ions or ions containing fluorine are selectively introduced into the region of the silicon substrate where the oxide film is to to be formed, followed by selective oxidation so as to form the oxide film on the aforementioned region where the

[0018]

In the following, the method for forming the element separating insulation film will be explained with reference to an application example of the first portion of the invention illustrated by the flow chart shown in Figure 2.

[0019]

As shown in Figure 2(1), by means of the thermal oxidation method, a pad silicon oxide film (12) with thickness of, for example, 10 nm, is formed on the surface of silicon substrate (11). Then, by means of the low-pressure CVD method, silicon nitride film (Si_3N_4) (13) with a thickness of 100 nm is formed. Then, after coating of a resist film, lithography is adopted to perform patterning, forming resist mask (14).

[0020]

Then, as shown in Figure 2(2), by means of dry etching, the portion of silicon oxide film (13) indicated by the double-dot-dash line is removed, forming oxidation inhibiting mask (15) by residual portion of silicon nitride film (13). In this case, pad silicon oxide film (12) may be left there. The aforementioned figure illustrates the case of etching of said pad siliccn oxide film (12). In the aforementioned dry etching, for example, a cassette type magnetron reactive ion etching device is used. The etching atmosphere is composed of octafluorocyclobutane (C_4F_8) with a flow rate of 5 sccm, oxygen (O_2) with a flow rate of 4 sccm, and argon (Ar) with a flow rate of 100 sccm. The pressure

of the etching atmosphere is selected at 2.7 Pa, and the RF power is selected at 1 kW. Then, oxygen ashing or wet processing is performed to remove resist mask (14).

[0021]

Then, as shown in Figure 2(3), fluorine gas or a gas containing fluorine is fed into the selective oxidation atmosphere to selectively oxidize the surface of silicon substrate (11), except the region covered with said oxidation inhibiting film (15), forming silicon oxide film (16). Said selective oxidation atmosphere may be made of oxygen (O_2) with a flow rate of 10 SLM, hydrogen (H_2) with a flow rate of 10 SLM, and fluorine (F) with a flow rate of 5 SLM. The oxidation temperature is set at 950°C. The aforementioned selective oxidation atmosphere may also be made of a gas mixture of oxygen (O2) and fluorine (F), or a gas mixture of steam and fluorine (F).

[0022]

Then, oxidation inhibiting mask (15) and pad silicon oxide film (12) are removed. Said oxidation inhibiting mask (15) is made of a silicon nitride film. For example, it can be removed using wet etching by means of hot phosphoric acid. Also, the pad silicon oxide film (12) may be removed using dry etching. Said dry etching operation may be carried out by dipping for 1-2 min in an aqueous solution of hydrofluoric acid with ratio of hydrofluoric acid to H_2O of about 1:100. By performing said dry etching, the upper layer of silicon oxide film (16) is also

removed. In this way, as shown in Figure 2(4), on the side of surface of silicon substrate (11), element separating insulation film (1) made of silicon oxide film (16) is formed.

[0023]

In the aforementioned application example of the first portion of this invention, oxidation of the surface of silicon substrate (11) is performed in an atmosphere made of a mixture of oxygen and hydrogen. Consequently, element separating insulation film (1) formed in this case is silicon oxide film (16) containing fluorine atoms. Consequently, the dielectric constant of element separating insulation film (1) can be reduced to about 3.0, depending on the content of fluorine in silicon oxide. Also, the amount of the fluorine atoms contained in said silicon oxide film (16) can be adjusted by controlling the flow rate of fluorine fed into the selective oxidation atmosphere.

[0024]

In the following, explanation will be made on the method for forming the element separating insulation film with reference to the flow chart shown in Figure 3 for the application example of the second portion of the invention. In this figure, the same structural parts are represented by the same part numbers as those adopted in Figure 2.

[0025]

Just as what is explained with reference to said Figures 2(1) and (2), as shown in Figure 3(1), pad silicon oxide film (12) (with film thickness of, for example, 10 nm) is formed on the surface of silicon substrate (11). On this film, silicon nitride film (13) (with thickness of, for example, 100 nm) is formed. In addition, after coating of a resist film, lithography is performed to form a resist mask (not shown in the figure). Then, by means of dry etching, the portion of silicon nitride film (13) indicated by the double-dot-dash line is removed, forming oxidation inhibiting mask (15) by the residual portion of silicon nitride film (13). In this case, pad silicon oxide film (12) (the portion indicated by one-dot-dash line) is etched. Then, oxygen ashing or wet processing is performed to remove the aforementioned resist mask.

[0026]

Then, as shown in Figure 3(2), selective oxidation is performed for the surface of silicon substrate (11), excluding the region covered with said oxidation inhibiting film (15) in a selective oxidation atmosphere made of oxygen and hydrogen, to form silicon oxide film (16) containing fluorine atoms. Said selective oxidation atmosphere may be made of oxygen (O_2) with a flow rate of 10 SLM and hydrogen (H_2) with a flow rate of 10 SLM, at an oxidation temperature of 950°C.

[0027]

Then, as shown in Figure 3(3), with oxidation inhibiting mask (15) made of said silicon nitride taken as an ion implantation mask, the ion implantation method is adopted to implant fluorine ions (F^+) into said silicon oxide film (16). The ion implantation condition is selected with an implanting energy of 30 keV and a dose of 10 P (peta) cm^{-2}.

[0028]

Then, oxidation inhibiting mask (15) and pad silicon oxide film (12) are removed. Removal of oxidation inhibiting mask (15) and pad silicon oxide film (12) is carried out using the same method as what explained in said Application Example 1. In this way, as shown in Figure 3(4), element separating insulation film (1) made of silicon oxide film (16) containing fluorine atoms is formed on the upper layer of silicon substrate (11).

[0029]

In said application example of the second portion of the invention, by means of the ion implantation method, fluorine ions are introduced into silicon oxide film (16), so that fluorine atoms are contained in element separating insulation film (1). Consequently, the dielectric constant of element separating insulation film (1) is reduced to about 3.0. Also, in the aforementioned ion implantation, the active region of silicon substrate (11) is covered with oxidation inhibiting mask (15) made of silicon nitride. Consequently, oxidation inhibiting mask

(15) becomes an ion implantation mask. Consequently, no fluorine ion is introduced into the active region. Also, the amount of the fluorine atoms contained in said silicon oxide film (16) can be adjusted by controlling the dose of the fluorine applied by ion implantation.

[0030]

In the following, with respect to the method for forming the element separating insulation film, the application example of the third invention will be explained with reference to Figure 4, a flow sheet of the operation. In this figure, the same part numbers are adopted to represent the same structural parts as explained in said Figure 2.

[0031]

Just as what explained with reference to said Figure 4(1), as shown in Figures 2(1) and (2), pad silicon oxide film (12) (with film thickness of, for example, 10 nm) is formed on the surface of silicon substrate (11). On this film, silicon nitride (Si_3N_4) film (13) (with thickness of, for example, 100 nm) is formed. In addition, after coating of a resist film, lithography is performed for patterning to form resist mask (14). Then, by means of dry etching, the portion of silicon nitride film (13) indicated by the double-dot-dash line is removed, forming oxidation inhibiting mask (15) by the residual portion of silicon nitride film (13). In this case, pad silicon oxide film (12) may be left there. What shown in the figure is the case when said pad silicon oxide film (12) is etched.

[0032]

Then, as shown in Figure 4(2), with resist mask (14) left there, said resist film and oxidation inhibiting mask (15) are taken as an ion implantation mask, and the ion implantation method is adopted to implant fluorine ions (F^+) into region (17) of silicon substrate (11) where the silicon oxide film is to be formed. The ion implanation condition is selected with an implanting energy of 40 keV and a dose of 10 P (peta) cm^{-2}. As a result, fluorine ions are introduced only to region (17) where silicon oxide film is to be formed, while no fluorine ion is introduced into the active region covered with resist mask (14).

[0033]

Then, by means of oxygen ashing or wet processing, resist mask (14) is remvoed. Then, as shown in Figure 4(3), in a selective oxidation atmosphere made of oxygen and hydrogen, selective oxidation is performed for the surface of silicon substrate (11) except the region covered by said oxidation inhibiting film (15), forming silicon oxide film (16) containing fluorine atoms. Said selective oxidation atmosphere may be made of oxygen (O_2) with a flow rate of 10 SLM and hydrogen (H_2) with a flow rate of 10 SLM. The oxidation temperature is set at 950°C.

[0034]

Then, oxidation inhibiting mask (15) and pad silicon oxide film (12) are removed. Using the same method as that explained in the first application example, oxidation inhibiting mask (15) and

pad silicon oxide film (12) are removed. As a result, as shown in Figure 4(4), element separating insulation film (1) made of silicon oxide film (16) is formed in the upper layer of silicon substrate (11).

[0035]

In said application example of the third portion of the invention, by means of the ion implantation method, fluorine is introduced into the region where the silicon oxide film is to be formed. Consequently, when this region is subjected to selective oxidation, silicon oxide film (16) containing fluorine is formed, and this silicon oxide film becomes element separating insulation film (1). Consequently, the dielectric constant of element separating insulation film (1) is reduced to about 3.0. Also, in the aforementioned ion implantation, the active region of silicon substrate (11) is at least covered with oxidation inhibiting mask (15) made of silicon nitride. Consequently, oxidation inhibiting mask (15) becomes an ion implantation mask. Also, when ion implantation is performed with the resist mask (14) left there, said resist mask becomes an ion implantation mask. Consequently, no fluorine ion is introduced into the active region covered with oxidation inhibiting mask (15). Also, the amount of the fluorine atoms contained in said silicon oxide film (16) can be adjusted by controlling the dose of the fluorine applied by ion implantation into silicon substrate (11).

[0036]

As explained in the above, in the aforementioned application examples for the first through third application examples, silicon oxide film (16) as element separating insulation film (1) is formed with fluorine atoms contained. Consequently, the dielectric constant of element separating insulation film (1) can be reduced to about 3.0. On the other hand, the silicon oxide film made of the conventional silicon dioxide has a dielectric constant of about 4.2. In this application example, for element separating insulation film (1), for which the dielectric constant is reduced to about 3.0, the film becomes equivalent to a conventional LOCOS oxide film with its thickness increased by about 30%.

[0037]

In this way, as the dielectric constant of element separating insulation film (1) is reduced, even when the thickness of element separating insulation film (1) is reduced, it is still possible to ensure the insulation needed for separating elements from each other. Consequently, as shown in Figure 5, when bird's beaks (31B) and (32B) (the portions indicated by the double-dot-dash lines) grown from element separating insulation films (1), (2) formed on the two sides of fine active region (21) (with width of, for example, 0.35 μm) formed on silicon substrate (11) are removed, the outer layers of element separating insulation films (1) and (2) (the portions indicated by one-dot-dash lines) are also removed. However, as the dielectric constant of element separating insulation films

(1) and (2) is reduced to about 3.0, there is still no increase in the parasitic capacitance by the element separating insulation film as compared with the element separating insulation film made of silicon oxide alone and without removing the surface layer. Consequently, there is no significant influence on the operation speed of the element.

[0038]

Effect of the invention

As explained above, for the element separating insulation film of this invention, the dielectric constant of the element separating insulation film can be reduced. Consequently, even when the thickness of the element separating insulation film is reduced, there is still no increase in the parasitic capacitance. Consequently, there is no decrease in the operation speed of the elements. Consequently, to the invention described in Claim 2, it is possible to form an oxide film in a state containing fluorine during selective oxidation. According to the invention described in Claim 3, it is possible to introduce fluorine into the oxide film after formation of the oxide film. According to the invention described in Claim 4, it is possible to form the oxide film in a state containing fluorine. Consequently, in any method, as fluorine atoms are contained in the oxide film, it is possible to form an element separating insulation film made of an oxide film having a low dielectric constant.

Brief description of the figures

Figure 1 is a schematic diagram illustrating the element separating insulation film of this invention.

Figure 2 is a flow chart of formation in the application example of the first invention.

Figure 3 is a flow chart of formation in the application example of the second invention.

Figure 4 is a flow chart of formation in the application example of the third invention.

Figure 5 is a diagram illustrating the function of this invention.

Figure 6 is a diagram illustrating the formation method in the conventional method.

Figure 7 is a diagram illustrating topics.

Brief explanation of reference symbols

1 Element separating insulation film
11 Silicon substrate
13 Silicon nitride film
15 Oxidation inhibiting mask
16 Silicon oxide film
17 Region where oxide film is to be formed

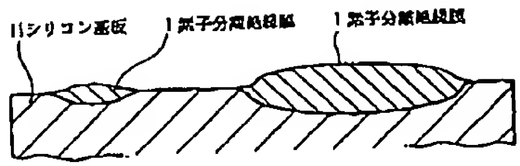

Figure 1. Schematic diagram illustrating the element separating insulation film of this invention.

Key: 1 Element separating insulation film
11 Silicon substrate

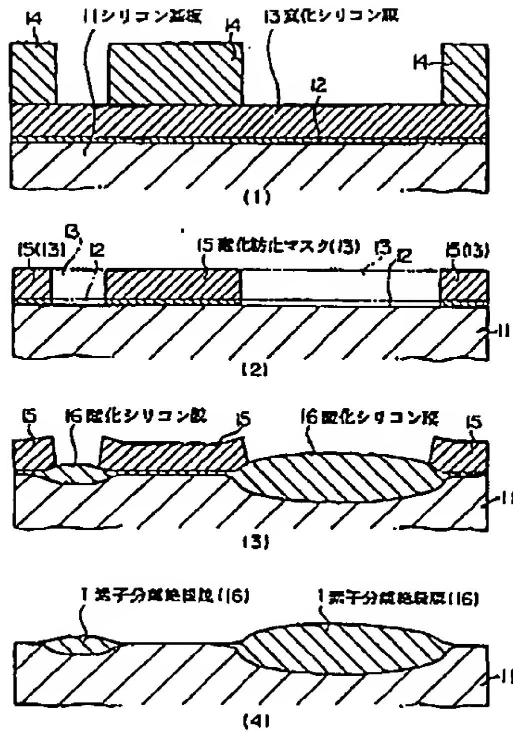

Figure 2. Flow chart of formation in the application example of the first invention.

Key: 1 Element separating insulation film (16)
11 Silicon substrate
13 Silicon nitride film
15 Oxidation inhibiting mask
16 Silicon oxide film

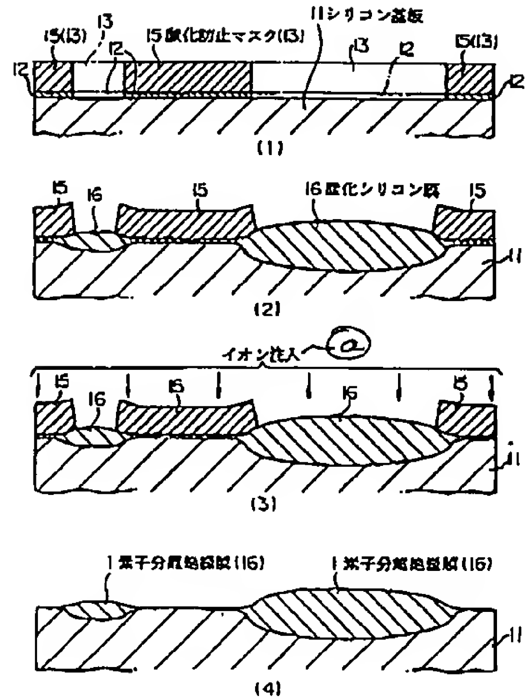

Figure 3. Flow chart of formation in the application example of the second invention.

Key: 1 Element separating insulation film (16)
11 Silicon substrate
15 Oxidation inhibiting mask
16 Silicon oxide film
a. Ion implantation

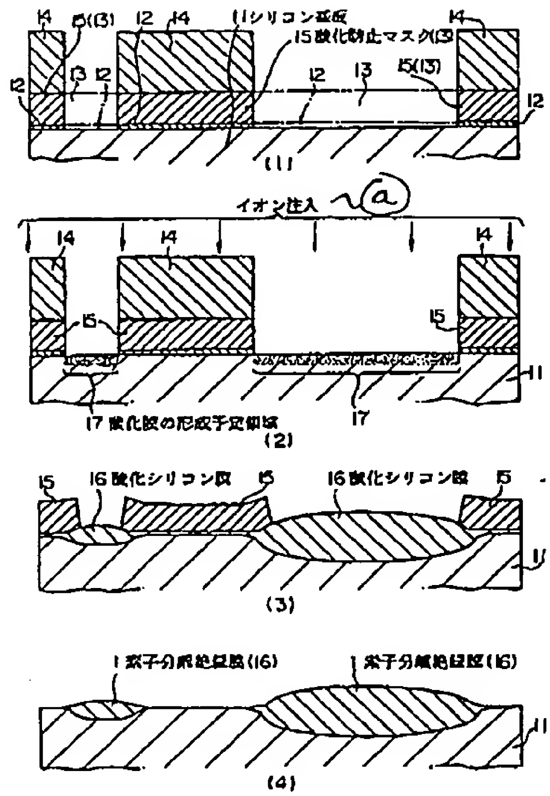

Figure 4. the third | Flow chart of formation in the application example of invention.

Key:
1 Element separating insulation film (16)
11 Silicon substrate
15 Oxidation inhibiting mask (13)
16 Silicon oxide film
17 Silicon oxide film
a. Ion implantation

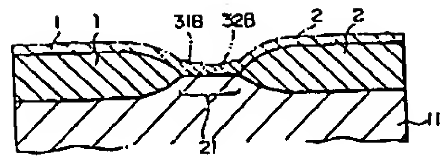

Figure 5. Diagram explaining a function of this invention.

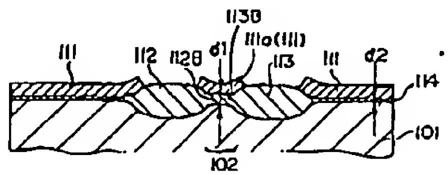

Figure 6. Diagram illustrating formation method of the conventional method.

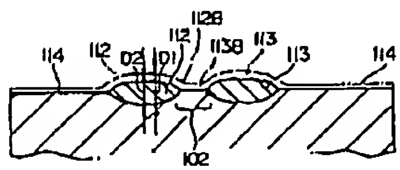

Figure 7. Diagram illustrating the problem to be solved.